NASA/TP–20240000373

A Minority Report Submitted as an Addendum to the Report of the Mars 2020 Organic Contamination Panel

Dr. Marc Fries
NASA Johnson Space Center, Houston, Texas

January 2025

NASA STI Program Report Series

Since its founding, NASA has been dedicated to the advancement of aeronautics and space science. The NASA scientific and technical information (STI) program plays a key part in helping NASA maintain this important role.

The NASA STI program operates under the auspices of the Agency Chief Information Officer. It collects, organizes, provides for archiving, and disseminates NASA's STI. The NASA STI program provides access to the NTRS Registered and its public interface, the NASA Technical Reports Server, thus providing one of the largest collections of aeronautical and space science STI in the world. Results are published in both non-NASA channels and by NASA in the NASA STI Report Series, which includes the following report types:

- TECHNICAL PUBLICATION. Reports of completed research or a major significant phase of research that present the results of NASA Programs and include extensive data or theoretical analysis. Includes compilations of significant scientific and technical data and information deemed to be of continuing reference value. NASA counterpart of peer-reviewed formal professional papers but has less stringent limitations on manuscript length and extent of graphic presentations.

- TECHNICAL MEMORANDUM. Scientific and technical findings that are preliminary or of specialized interest, e.g., quick release reports, working papers, and bibliographies that contain minimal annotation. Does not contain extensive analysis.

- CONTRACTOR REPORT. Scientific and technical findings by NASA-sponsored contractors and grantees.

- CONFERENCE PUBLICATION. Collected papers from scientific and technical conferences, symposia, seminars, or other meetings sponsored or co-sponsored by NASA.

- SPECIAL PUBLICATION. Scientific, technical, or historical information from NASA programs, projects, and missions, often concerned with subjects having substantial public interest.

- TECHNICAL TRANSLATION. English-language translations of foreign scientific and technical material pertinent to NASA's mission.

Specialized services also include organizing and publishing research results, distributing specialized research announcements and feeds, providing information desk and personal search support, and enabling data exchange services.

For more information about the NASA STI program, see the following:

- Access the NASA STI program home page at http://www.sti.nasa.gov

.

NASA/TP–20240000373

A Minority Report Submitted as an Addendum to the Report of the Mars 2020 Organic Contamination Panel

Dr. Marc Fries
NASA Johnson Space Center, Houston, Texas

National Aeronautics and
Space Administration

Johnson Space Center
Houston, Texas

January 2025

Available from:

NASA STI Services / Mail Stop 050
NASA Langley Research Center
Hampton, VA 23681-2199

A Minority Report
Submitted as an Addendum to the Report of the Mars 2020 Organic Contamination Panel

Dr. Marc Fries
NASA Johnson Space Center, Houston TX
marc.d.fries@nasa.gov

An Addendum to:

Summons, R. and Sessions A. (co-chairs), Allwood A., Barton H, Beaty D., Blakkolb B., Canham J., Clark B., Dworkin J., Fries M., Lin Y., Mathies R., Milkovich S., Steele A., "Report of the Mars-2020 Organic Contamination Panel", v.10, 03 Jul 2014

And:

Summons, R.E., Sessions, A.L., Allwood, A.C., Barton, H.A., Beaty, D.W., Blakkolb, B., Canham, J., Clark, B.C., Dworkin, J.P., Lin, Y., Mathies, R., Milkovich, S.M., and Steele, A. (2014) Planning considerations related to the organic contamination of martian samples and implications for the Mars 2020 rover. *Astrobiology* **14**, in press, doi:10.1089/ast.2014.1405.

Summary

This Minority Report (MR) presents seven findings in addition to or contrary to the main OCP report:

1) Contamination control for the Mars 2020 cache must be strict. Mars' surface is known to be organics-poor from laboratory studies, Mars meteorite analyses, and from four previous NASA missions. It is imperative that contamination control measures are enacted that enable reliable and robust detection of potential biomarker compounds at the ppb level.
2) Since Mars 2020 is a sample return mission and analyses of samples in the returnable cache are expected to occur after return to Earth, positive controls are not recommended for flight on Mars 2020 unless a compelling case can be made for their use.
3) The findings of previous panels dedicated to organic compound analysis in martian samples (OCSSG, ND-SAG, SDT) recommend TOC limits between 10-40 ppb. The MR finds that the lower limit of 10 ppb is recommended and that insufficient justification is given by the OCP Panel Report (PR) to raise the TOC limit to 40 ppb.
4) Analytical capability is sufficiently advanced that analytical capability is an irrelevant consideration with respect to differentiating between 10 and 40 ppb TOC.
5) Perceived contamination control challenges are an irrelevant consideration for raising the TOC contamination limit from 10 to 40 ppb since those challenges, and the procedures to ameliorate them, will exist regardless of whether the limit is 10 or 40 ppb.
6) The "dilution cleaning" method has not been adequately proven for utilization on the Mars 2020 mission. Shortcomings have been identified in terms of peer review, method verification, analytical and testing approach, application to space flight hardware, and performance under martian conditions. The method should be revisited and independently tested using statistically and analytically robust methods, and scrutinized in a rigorous peer review process.
7) The Mars 2020 mission claims considerable heritage from the Mars Science Laboratory (MSL) mission, but MSL contamination control efforts contain significant errors and implementation discrepancies that would imperil the Mars 2020 caching mission were they repeated. A standing contamination control panel should be formed to provide independent oversight for the Mars 2020 mission.

Table of Contents

1. Rationale for a Minority Report

The Mars 2020 Organic Contamination Panel (OCP) was chartered with three principal tasks, paraphrased here as 1) define organic contamination-related terms, 2) propose a set of organic contamination limits for the Mars 2020 sample cache, and 3) evaluate the Mars 2020 contamination control plan in its current state and offer suggestions. A panel of ten members, two co-chairs and a suite of ex-officio members was convened to discuss these tasks and generate a report. The tasks presented to the board are detailed and difficult by nature, and disagreements are a near-certainty among the panel members. While the panel chairs sought to accommodate the breadth of opinion offered by the panel members, it was always possible that the report would be unable to express the range of scientific opinions held by the board members. The Minority Report (MR) presented here serves the goal of encompassing and expressing the scientific opinions that are not contained in the OCP panel report (PR). The author of the MR does not intend to disparage, discount, or impugn the motives of the other OCP panel members, but respectfully offers the following scientific perspective for consideration.

To take a broader view, Mars 2020's returnable cache is an important step towards Mars sample return. Mars sample return is both scientifically important in its own right, and it is a necessary step that must precede manned Mars missions. It must come first for both human hazard mitigation and because there is a vital scientific need to understand the native state of Mars before human missions transport a large body of diverse terrestrial organisms to the martian surface. A great deal of future effort hinges upon successful Mars sample return. However, we must not underestimate the titanic difficulty of retrieving minimally contaminated samples from Mars. *Proficient organic contamination control is absolutely vital to achieve mission success in Mars sample return missions.* This Minority Report is offered with full knowledge of the importance of the Mars 2020 mission. It is also offered with profound concern for achieving Mars 2020 mission goals, and with the understanding that a sober and realistic appraisal is required of the towering scientific and engineering challenges associated with returning scientifically useful samples from the severely organics-depleted martian surface. Successful Mars sample return is possible, but only with strict contamination control.

2. Background: Justification for Strict Contamination Control in the Mars 2020 Cache

The NASA Mars 2020 mission will collect samples for a returnable cache (NASA SDT Report, Section 3.4) and there will be an element of past life detection (NASA SDT Report, Section 2.2.2). Therefore the Mars 2020 mission is unprecedented in NASA experience in several important ways, namely that it is the first NASA mission with the potential to return samples from Mars and is also the first NASA sample return mission to specifically search for signs of life. Contamination control should be equally unprecedented due to the nature of the mission, of sample return

missions in general, and the nature of the target materials. The following reasons are given in support of the assertion that contamination control for the Mars 2020 cache must be extraordinarily strict.

Paucity of Martian Organics: Based on previous laboratory studies, analyses of martian meteorites, and missions, we can expect organic compounds to be sparse in returned martian material. To put the reasonably expected amount of martian organics in perspective, studies have shown that the rare earth element neodymium is about *five times more plentiful* than amino acids in a typical martian meteorite (see Appendix A). And even that number is an upper limit, as the measured values of amino acids contain a substantial terrestrial contamination component to the extent that the actual amount of amino acids may be zero (see Appendix A). Previous NASA missions also indicate that martian organics are a rarity. Four NASA missions with the capability to detect trace amounts of carbon have sampled the martian surface at a range of latitudes: Viking 1, Viking 2, Mars Phoenix, and Mars Science Laboratory (MSL). The results of those missions are consistent. Organic materials in the martian near-surface are extremely scarce, and even the trace carbonaceous compounds identified (e.g. chloromethane) have been altered to the point that their pre-analysis composition is lost [Klein *et al* 1976, Benner *et al* 2000, Boynton *et al* 2009, Ming *et al* 2014]. Viking 1 and 2 were capable of ppb-level detection of a range of organic compounds but only detected trace amounts of chloromethane and dichloromethane, possibly due to alteration by martian oxidants [Biemann *et al* 1976, Navarro-Gonzalez *et al* 2006, Navarro-Gonzalez *et al* 2011]. The Mars Phoenix lander also reported detection of CO_2 that may have originated from "organic molecules that are converted to CO_2 by oxidants in the soil" [Boynton *et al* 2009]. MSL has repeated the Viking findings by detecting chloromethane and dichloromethane, but the source of these compounds is described as "not definitively of martian origin" [Ming *et al* 2014]. None of the four missions have unambiguously detected native martian organic compounds, despite each mission featuring ppb-level sensitivity to organic compounds [Klein *et al* 1976, Boynton *et al* 2009, Ming *et al* 2014]. Therefore, for Mars 2020, contamination control must be capable of permitting at least ppb-level analyses of organic species in the returned samples. The paucity of organics near the martian surface is also indicated by laboratory studies. Loes ten Kate *et al* (2005) predicted that amino acids would be "likely to be below the ppt level" at the martian surface due to ambient radiation, based on a laboratory simulation study and other authors have likewise predicted that the martian surficial radiation environment will severely degrade near-surface organic material [Oro and Holzer 1979, Kminek and Bada 2006, Summons *et al* 2011 and references therein]. Stoker and Bullock (1997) likewise found that ambient radiation would destroy all organic molecules in the martian near-surface to such an extent that no oxidizers are required to explain the Viking non-detection of organics. And Kanavarioti and Mancinelli (1989) found on the basis of chemical degradation kinetics that ancient amino acids could only survive in the martian sub-surface.

Potential Biosignatures as a Fraction of TOC: The OCP discussed the findings of the Mars Sample Return Science Steering Group 2 (MSR-SSG2), particularly with regard to that group's rationale for assessing stringent contamination control requirements. To quote the OCP report, page 18:

> "…in an effort to set a lower bound on what might be required for analyses of Martian rocks, the group considered analogous organic-poor rocks on Earth, as follows. Oxidized red sandstones and mudstones ('redbeds') commonly contain 0.10 to 0.01 weight percent total organic carbon (TOC). Of this, typically less than 10 μg/g is extractable bitumen, and sometimes as low as 1 μg/g. Major compound classes, such as aliphatic hydrocarbons, often represent just 1% of that total extract, or 10 ng/g. Individual biomarker molecules, for example n-alkanes and hopanes, are themselves typically only 1-10% (or less) of aliphatic hydrocarbons, and so present at 0.1–1.0 ng/g (Macpherson et al., 2005, pp 29-30). Inferring that similarly low levels might be present in returned Martian samples, the MSR-SSG2 proposed organic contamination thresholds that were lower than those of the OCSSG by a factor of 4, i.e. 10 ng/g TOC, and as low as 0.25 ng/g amino acids. Critical to their evaluation and conclusions is the assumption that terrestrial TOC-poor rocks are representative of what we might find on – and return from – the surface of Mars. The validity of this assumption was not explicitly discussed by the SSG2 report, and was questioned by several panelists in the OCP."

No reason is given in the OCP why the validity was questioned, or what the OCP decided as a group. This is an important summary, as this MR believes that the MSR-SSG2 logic stated above is sound and serves as a solid recommendation for contamination limits (more on this in Section 4 "The 40 ppb Limit"). Some OCP members disagreed with the MSR-SSG2 because, as stated in an earlier version of the OCP report (v.10), "these rocks contain very little organic carbon mainly because of the vigorous activities of aerobic, heterotrophic microbes in the original sediments". The cause of carbon paucity is irrelevant, and the redbed example is important because its carbon paucity is an analogue of what can be expected for martian samples – a biosignature-bearing rock that was depleted in carbon following deposition. The redbed example illustrates the relationship between TOC and potential "biomarker" abundance, and that *biomarker abundance is not synonymous with total carbon abundance*. The redbed description begins by stating a TOC content of 0.1-0.01 wt.% C and describes how the organic carbon biomarkers of astrobiological significance occur at much lower levels of around 1.0-0.1 ppb (ng/g) each, as stated above. Therefore the individual biosignature compounds appear at a ratio of around 1:1E^{6} versus the total organic carbon abundance (See Appendix B). Even if this value were in error by several orders of magnitude, the fact remains that the actual amount of potential biosignatures is a small fraction of TOC. This ratio is emblematic of natural samples to include martian materials placed in the returnable cache, and so background contamination must be constrained to a very small fraction of the expected TOC in order to allow analysis of the potentially biogenic fraction.

Extended Mission Considerations: Sample return missions are, by nature, missions that generate science returns long after the last piece of mission hardware ceases to function. In the event that the cache is returned, samples from the Mars 2020 mission will enjoy an "extended mission" lifetime along the lines of that of the

Apollo sample collection. While the actual Apollo flights ended 42 years ago, Apollo samples continue to be examined by researchers around the world as new techniques and hypotheses evolve. At the time of this writing some *85% of the Apollo collection has still not yet been loaned out for research* (Dr. Ryan Ziegler, Apollo collection curator, personal comm.) and so the Apollo collection will continue to serve scientific needs for generations to come. This means that failing to enact sufficiently stringent contamination control measures in the early stages of Mars 2020 will negatively affect research efforts for generations to come, long after the 2020 rover ceases to function.

Finding MR1: Contamination control for the Mars 2020 cache must be strict. Mars' surface is known to be organics-poor from laboratory studies, Mars meteorite analyses, and from four previous NASA missions. It is imperative that contamination control measures are enacted that enable reliable and robust detection of potential biomarker compounds at the ppb level.

3. Important Agreements Between the MR and OCP Panel Report

The MR expresses particular agreement with the following points from the PR:

1. The 1 ppb limit on all Tier 1 compounds, as described in the PR.

2. The 10 ppb limit on all Tier 2 compounds, as described in the PR.

4. Positive Controls

The OCP is unclear on whether positive controls are recommended or not for Mars 2020. Page 58 of the OCP report contains the following statement:

> "*As an example, Phoenix flew an organic-free ceramic blank that was to be used to characterize the cleanliness of the sampling system by using the Thermal Evolved Gas Analyzer to detect organic molecules (Ming et al., 2008). MSL was prepared to use this strategy to control its sampling and analysis operations by means of what is referred to as the Organic Check Material (OCM) (Conrad et al. 2012), although as a practical matter, the OCM has not been sampled on Mars as of this writing (Fig. 16). The OCM is a block of ceramic (a non-Mars material) that was fired at high temperature to drive off all organic molecules. (The OCM was then doped with a single non-Mars organic molecule, so that it can serve both as a positive and a negative control standard).*"

It is not clear from the OCP statement whether or not the OCP formally recommends the use of positive controls since examples of both negative controls (the Mars Phoenix organic-free ceramic blank) and a positive control (the MSL OCM). The purpose of positive controls such as the MSL OCM is to provide a known amount of a known compound to calibrate instrumental response of instruments on board the MSL rover. For Mars 2020, however, the principal analyses will be performed in terrestrial laboratories and positive controls can be provided for those instruments at that time. If a positive control is brought with the Mars 2020 mission and it is stored in the returnable cache, there is a probability that the martian samples will be contaminated by leakage from the positive control. The MR recommends against the use of positive controls for the Mars 2020 mission unless a compelling case can be made for their use.

Finding MR2: Since Mars 2020 is a sample return mission and analyses of samples in the returnable cache are expected to occur after return to Earth, positive controls are not recommended for flight on Mars 2020 unless a compelling case can be made for their use.

5. The 40 ppb TOC Limit

The MR disagrees with the OCP Finding #17, p. 50 (Section 4.3.2) in OCP PR, which states, "We propose a limit of < 40 ng/g (ppb) for total organic carbon (TOC) contamination in the returned samples." This recommendation falls under the purview of Task #2 in the OCP charter, namely to, "Propose one or both of two kinds of limits for Earth-sources organic contamination on the potential returned martian samples at the point in time when they are first analyzed for organic molecules: either a) total organic contamination or b) total unrecognized organic contamination (i.e. contamination above measured blank levels".

The strategy the OCP agreed upon was to set three limits on organic contamination: an overall TOC limit, limits for "Tier 1" compounds of astrobiological significance, and upper limit on individual "Tier 2" compounds which are defined as everything that isn't in the Tier 1 list. Limits proposed by the OCP are:

- TOC limit of 40 ppb
- Tier 1 limit of 1 ppb per compound
- Tier 2 limit of 10 ppb per compound

The MR concurs with the Tiers 1 and 2 limits. Available data from past and current Mars landed missions indicates that organic compounds of astrobiological significance, if they are present, may be expected at the single-ppb limit. The reasons for this are spelled out in detail in the OCP report and will not be repeated here.

The MR disagrees with the TOC limit of 40 ppb for two reasons:

1. The limit of 40 ppb constitutes an increase in TOC limit over that suggested by previous panels that investigated this subject, to such a degree that the higher limit might significantly affect the mission's ability to meet science goals.
2. The 40 ppb limit was reached with an emphasis on analytical capabilities and perceived contamination control limitations that is not justified. The scientific need for a specific limit should be the driving factor, and if technological limitations do exist then they should be addressed in the course of the mission with a technology development program. This approach has been used successfully with previous NASA sample return missions such as Genesis and Stardust.

Reason 1 Explained – Raising the TOC Limit:

Previous panels have specifically addressed the issue of limits on organic contamination in Mars samples in order to facilitate successful analysis of native martian carbonaceous material. We can reasonably simplify the problem by stating that the previous panels decided on a TOC limit of between 10 and 40 ppb of organic carbon in the samples themselves. However it is useful to understand their descriptions in detail so those are discussed here:

- OCSSG (Mahaffy *et al* 2003): The OCSSG panel was chartered by the Mars Program Office at NASA HQ specifically to study "the steps necessary to reduce the potential impacts of terrestrial contamination on *in situ* Mars measurements" (p. 2, Mahaffy *et al* 2003). The OCSSG discussed placing organic contamination limits "…below 1-10 parts per billion in Mars samples…"(p.7, *ibid*) for the study of meteorite-delivered organic species, and stated that the "total molecular carbon contamination allowed could be substantially higher (for example, 40 ppb) if the contamination by specific critical species or classes was maintained at dependably constant levels." The next sentences in the document summarize the OCSSG finding on organic contamination limits for biosignature studies specifically: "Although extinct or extant life on Mars has the potential to leave signature organic material in either much higher abundance than the parts per billion levels discussed above, the OCSSG concluded that a definitive search for such signatures could be implemented on MSL by **maintaining terrestrial contamination below levels of 1-10 ppb for relevant biomarkers**" (MR's emphasis). Therefore, OCSSG suggested limits of "below 1-10 ppb" for individual compounds, similar to the Tier 1 compounds defined by the OCP. The closest OCSSG comes to setting a TOC limit is their "total molecular carbon" limit of "…(for example, 40 ppb)…" The terminology used by the OCSSG is the least specific of all of the panel findings, but was referred to by the later studies as described below.

- ND-SAG (MacPherson *et al* 2008): In 2008, the Mars Exploration Program Analysis Group (MEPAG) chartered the Next Decade Science Analysis Group (ND-SAG), and the Mars Sample Return Science Steering Group 2 (SSG 2) devised a set of recommended limits for organic contamination in future sample

return missions. ND-SAG recommends that, "while OCSSG specified contamination levels for organic molecules would be adequate for a subset of the samples where organics analysis is not the primary objective, **lower thresholds by a factor of 4 or more are desired … where organics analysis would be a primary investigation** (MR's emphasis)." In other words, for missions such as Mars 2020 where life detection is a primary concern, the overall TOC limit should be at least four-fold lower than that set by OCSSG.

- SDT (Mustard *et al* 2013): The Mars 2020 Science Definition Team was chartered by MEPAG to define concepts and scientific goals specifically for the Mars 2020 mission. The SDT specifically addressed organic contamination in the caching system, designating organic contamination as a "High Impact Area for SDT Consideration" (p. 89, Mustard *et al* 2013) and devoted nine pages of the SDT document to discussion of organic contamination. Their summary in Table 6-3 incorrectly states that OCSSG set a limit of 40 ppb (see references above). **The SDT recommendation is a baseline TOC limit of 10 ppb, and a threshold limit of 40 ppb**. The SDT document is the most clearly stated document, although "threshold limit" is not clearly defined.

The previous panels (OCSSG, ND-SAG, 2020 Rover SDT) as well as the OCP itself agree that measurements are needed *at the ppb level* in order to detect native martian organic compounds in martian materials, either on the martian surface or in returned samples. The three panels differ somewhat in implementation limits, with options ranging from "about 40 ppb total molecular carbon" (OCSSG), to a fourth that value or less (ND-SAG), to a "baseline" of 10 ppb with a "threshold limit" of 40 ppb (SDT). There are a few reasons to prefer the lower value, among them analytical best practice. The most important reason is to better ensure mission success for the Mars 2020 rover cache given the paucity of martian organics as detailed previously. For these reasons stricter contamination control requirements are favored, and raising the TOC limit from 10 ppb to the OCP's suggested 40 ppb is not something to enter into lightly considering the OCP expects individual compounds of interest to be present around the single-ppb range as stated: "at least some, and perhaps most, martian rocks would contain important organic compounds at levels of a few to tens of ng/g" (OCP PR p.66). The PR states, "The panel unanimously agreed that setting lower TOC limits would be very beneficial for the reduction in numbers and levels of individual organic contaminants, and for the decreased probability of significant interferences with scientific measurements" (Section 4.3.2, p.50 OCP PR). The rationale presented in the OCP report for raising the TOC limit to 40 ppb is insufficient considering the magnitude of the potential harm done.

Finding MR3: The findings of previous panels dedicated to organic compound analysis in martian samples (OCSSG, ND-SAG, SDT) recommend TOC limits between 10-40 ppb. The MR finds that the lower limit of 10 ppb is recommended and that insufficient justification is given by the OCP Panel Report (PR) to raise the TOC limit to 40 ppb.

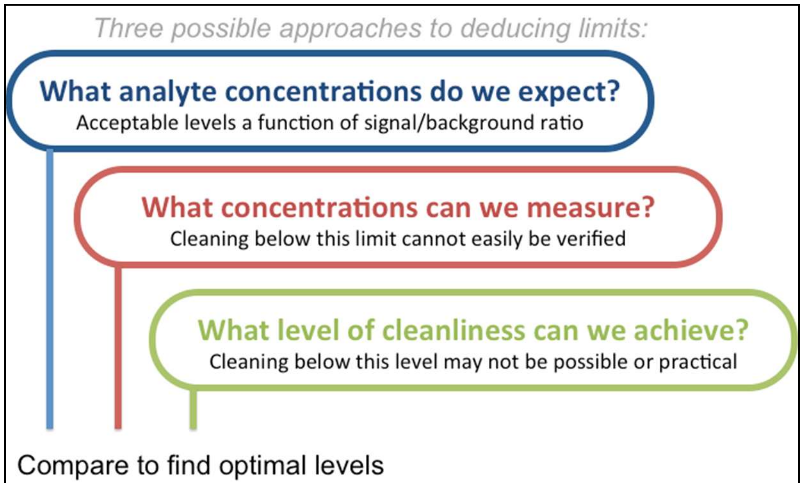


Figure 10 from OCP PR, showing the three criteria used to determine contamination limits by the panel. The MR disagrees that analytical capability and perceived contamination control challenges should be determining factors for contamination limit recommendations.

<u>Reason 2 Explained</u> – An Unjustified Emphasis on Perceived Analytical and Technological Limitations:

Previous panels devised contamination control limits for martian samples based on their scientific understanding of the nature of martian materials. The OCP PR has deviated from this standard by adding two more factors: analytical capability and technical feasibility (Section 4.2.2, Figure 10 in the OCP PR, p.36). Analytical feasibility is a non-factor in the difference between 10 and 40 ppb. In the course of other missions such as Genesis, Stardust, and OSIRIS-REx, the development of a contamination control implementation plan has always required technology development to meet mission requirements and has never been a limiting factor in mission execution. Neither analytical capability nor contamination control development should be considered as limiting factors when defining scientific recommendations for the Mars 2020 mission.

<u>Analytical Capability</u>, or "What concentrations can we measure?" in Figure 10 (above), is described in Section 4.2.2.2. Two reasons are given for considering this factor:

1. The OCP states, "<u>First, it is not feasible to set requirements that are below the detection limit of any analytical method</u>" (OCP PR p.41). The MR disagrees that this is a valid consideration for selecting between 10 and 40 ppb. To the best of the MR's knowledge, any instrument capable of analyses on the order of 40 ppb is also capable of 10 ppb. For example, commercial TOC instruments exist today with limits of detection (LOD) in the 0.01 ppb range. (i.e. Sievers 500 RLe or other "semiconductor grade" TOC instruments). The PR appears to agree with this, stating, "We adopt 1 mg/g as a representative value" for limits of detection

for the compounds of interest (*ibid*). The MR finds that the feasibility-based argument is without merit with respect to differentiating between TOC levels of 10 and 40 ppb.

2. The PR states in Section 4.2.2.2 that "<u>there would be little practical benefit in protecting analyte concentrations that are themselves too low to measure</u>". The OCP panel's intent with this statement is not entirely clear. Analytes that are present in concentrations too low to measure are, by definition, absent to within a known LOD but their absence may still have profound scientific ramifications (e.g. the apparent absence of meteorite-derived carbonaceous material on Mars' surface [Benner *et al* 2000]). The TOC and Tier 1&2 limits define clearly what the panel has decided to protect. Analyte concentrations should be protected to a LOD defined by the science needs of the mission, and that is constrained by OCP and other panels as either 10 or 40 ppb for TOC.

Finding MR4: Analytical capability is sufficiently advanced that analytical capability is an irrelevant consideration with respect to differentiating between 10 and 40 ppb TOC.

<u>Perceived Contamination Control Challenges</u>, or "What level of cleanliness can we achieve?" in Figure 10 above:

The OCP PR asks, "what levels of background contamination can be achieved using current technology"? (p. 41, Section 4.2.2.3 OCP PR). The PR then describes a series of complicating factors, given here with rebuttal:

1. "Contamination varies widely in space and time …etc." (*ibid*) This problem is overcome with a statistical approach to contamination control, as is common practice. A series of proxy caches can be batch-cleaned, and samples analyzed to determine the statistical cleanliness level of the batch. This approach was discussed in detail by the OCP panel but is not discussed in the PR.

2. "Second, eliminating contamination is difficult and time consuming, and so typically is driven to the levels that are needed, rather than those that are technologically possible" (*ibid*). The MR agrees with this statement in principle. The "levels that are needed" are the Tier 1&2 levels as defined in the OCP document, and a TOC limit of 10 ppb as shown in previous panels and in the science results of the four previous landed missions described earlier (Vikings 1 and 2, Mars Phoenix, MSL). The statement that proper contamination control will be "difficult and time consuming" does not add to the discussion in a constructive and technical manner.

3. "Third, quantitative background concentrations are not often reported" (p.42 *ibid*). It is standard practice in analytical chemistry and most other fields for quantitative reporting of background levels complete with a statistical treatment of results.

4. “Fourth, methods of reducing contamination are often specific to the particular analytes of interest, and so it is unclear whether it is possible to simultaneously achieve reported limits for all analytes of interest” (*ibid*). The OCP PR has defined the contaminants of interest, and it is possible on Earth to batch-clean and batch-sample caching equipment in order to spread the analyses over a series of cache components. Also, there will certainly be a period of methods development in the contamination control preparation for the Mars 2020 mission just as there are with other missions, and issues such as this can be addressed just as they were for Genesis, Stardust, OSIRIS-REx and others.

In short, the four factors given in the OCP PR have been handled in the course of previous missions and there is no new, compelling reason to believe that they represent insurmountable hurdles for Mars 2020. The Mars 2020 mission will require development of contamination control techniques just as Genesis [Burnett *et al* 2003], Stardust [Sandford *et al* 2010], OSIRIS-REx and other missions have, to include technology development. It is not reasonable to limit scientific recommendations based on a contamination control development process that will occur regardless of the actual values recommended. Somewhat confusingly, the OCP concludes Section 4.2.2.3 by agreeing that the considerations are not significant: “We thus foresee no significant difficulties in achieving the levels of cleanliness indicated by the considerations in the preceding sections”. The MR fundamentally disagrees that perceived technical feasibility is a valid factor in setting the contamination control limits needed to achieve the science goals of the mission.

Finding MR5: Perceived contamination control challenges are an irrelevant consideration for raising the TOC contamination limit from 10 to 40 ppb since those challenges, and the procedures to ameliorate them, will exist regardless of whether the limit is 10 or 40 ppb.

Additionally, to take a larger view, *advanced sample return is the way forward for NASA missions into the foreseeable future.* Sample return missions from organic-rich, astrobiologically important bodies are currently considered to be of high scientific importance; specifically Enceladus, Europa, and Ceres. Each of these worlds features liquid water and sample return are currently considered to fall under the same Planetary Protection Category V- Restricted Return criteria required for the Mars 2020 returnable cache (Conley C., personal comm.). Developing the technology and techniques for ultra-clean sample return is an emerging NASA need that will transcend the needs of Mars 2020 alone.

6. Discussion of “Dilution Cleaning”

Dilution cleaning (DC) is a contamination remediation technique that was utilized on MSL and may be utilized in the Mars 2020 mission, and as such it must be discussed as per part 3 of the “Statement of Task” in the OCP charter: “Evaluate draft

Mars 2020 mission … draft verification methodologies", and section 3a, "Propose modifications to the draft Mars 2020 requirements and verification methodologies as needed". In OCP email traffic, some panel members expressed the opinion that DC may not be an operationally useful strategy for Mars-2020, and the OCP PR states, "…the dilution cleaning process appears not to be available to M-2020" (p.48). Confusingly, however, the next paragraph advocates DC with the statement that "current design ideas for [Mars 2020) drilling apparatus include both reusable and single-use designs. Re-usable drill strings have the advantage of being able to undergo 'dilution cleaning'". Also, Table 9 on page 100 states that Mars 2020 differs from MSL in that Mars 2020 features "Expected minimal use of dilution cleaning" but does not exclude DC from Mars 2020, and a similar reference appears on p.107. The OCP PR's discussion of DC is inconsistent, but the MR finds that DC must be discussed due to its potential role in cache contamination control.

DC played an important role in the MSL mission. The OCSSG report recommended that all surfaces in the MSL sample handling chain be cleaned to a maximum of 1 ng/cm^2 organic contamination as non-volatile residue (NVR) (OCSSG report, Table 3, p.15), or IEST-STD-CC1246E level R1E-1 (formerly designated level A/10). Instead, the MSL mission obtained a waiver and the instituted requirement was for a maximum of 100 ng/cm^2 (OCP PR p.14). The limit was applied at two orders of magnitude greater than that suggested by OCSSG because DC was applied as "a central part of MSL's strategy" (OCP PR p.11).

Dilution cleaning is described in Anderson *et al* (2012). The paper describes DC as a method for decreasing the amount of surficial contamination and demonstrates the technique using a specially constructed test chamber. A controlled amount of *bis*(2-ethyl-hexyl) phthalate (or DOP) was coated onto one surface of the chamber, and an aliquot of clean KBr powder was added to the chamber. The chamber was exposed to vibration for a prescribed period of time, the KBr was removed, and the amount of DOP present in the KBr measured by transmission FTIR. Results indicate that the DOP concentration decreased each time a clean sample of KBr was agitated in the test chamber. Review of the DC technique as described in Anderson *et al* (2012) reveals a number of questions about the validity of the technique, described below. The MR finds the following problems with the DC approach:

Problems with DC:

1) <u>Scientific Maturity</u>:
   a. <u>Insufficiently Robust Peer Review</u>: The journal *Review of Scientific Instruments*, in which Anderson *et al* (2012) was published, maintains a policy of utilizing a single reviewer where possible. The *Rev. Sci. Inst.* website states, "Manuscripts submitted are first screened by the editors, and those within the scope of the Journal are sent to an expert referee for evaluation. A manuscript may be sent to a second reviewer as deemed necessary by the Associate Editor or Editor." It is not clear if Anderson *et al* (2012) received peer review by the standard single reviewer or if a second reviewer was added, but in the event a single reviewer was utilized, this comprises only the bare minimum to achieve "peer review". Given the pivotal role DC performs in MSL and potentially Mars 2020, the MR finds

that Anderson *et al* (2012) did not receive peer review that is sufficiently robust to justify its use as a remediation technique.

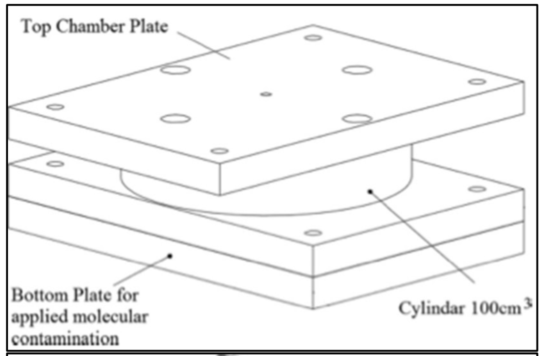
b. Lack of Independent Verification: As of October 2014, no peer-reviewed papers that refer to Anderson *et al* (2012) describe validation of the DC technique by other institutions. Searches using multiple search engines also did not reveal any instances where DC has been validated by other laboratories. The scientific veracity of DC would be dramatically improved by independent verification of the technique, which is standard practice across scientific and engineering disciplines. Also, the paper refers repeatedly to the model used to estimate contamination transfer to samples, yet no detailed description is provided for this model.

2) Analytical/Laboratory Approach:

a. Only One Contaminant Tested: Anderson *et al* (2012) only investigates one compound (DOP) and there is significant uncertainty in how well this method suffices for other important compounds, such as the list of Tier I compounds (DNA, dipicolinic acid, PAHs, etc.). At present there is insufficient information to accurately predict the behavior of Tier I (or other) compounds under DC treatment, dramatically hindering Mars 2020 contamination control efforts for the Tier 1 compounds. The use of a single compound also renders the data unsuitable for predicting TOC contamination behavior under DC treatment. This is because TOC is composed of all chemically available organic compounds in a given environment, and the preponderance of those compounds feature different adhesion properties than DOP.

b. Only One Surface Material Tested: Anderson *et al* (2012) uses only one test chamber material, titanium. The transfer efficiencies of contaminants from other, more reactive materials such as aluminum and stainless steel have not been demonstrated. This makes the results from Anderson *et al* (2012) difficult to apply to other materials in the Mars 2020 sample handling chain.

c. <u>Analytical approach</u>: Anderson *et al* (2012) reports a total of 25 measurements in the paper to interrogate five experimental runs with five experimental conditions (four dilutant agitation runs and one measurement of the post-run chamber interior), while changing three experimental parameters (basalt vs. KBr, mass of dilutant used, agitation time). The number of measurements is insufficient to generate statistically meaningful descriptions of contaminant behavior, such that the influence of each of the three major experimental parameters can be independently described. By contrast, Armbruster and Pry's 2008 heavily cited paper on "Limit of Blank, Limit of Detection and Limit of Quantification" recommends no fewer than 60 analyses each for each data point in demonstrating a new technique. Also, ASTM standard E2857 "Standard Guide for Validating Analytical Methods", specifies a detailed approach to include determination of limit of quantification, limit of detection, bias, precision, statistical treatment of results and other necessary factors that are absent in Anderson *et al* (2012). Additionally, the measurements are apparently single FTIR measurements instead of the best practice of at least triplicate measurements, as neither mean nor standard deviation values are reported. Blank values are likewise unreported, although the text states "(b)lanks of evaporated dichloromethane and rinses of the text hardware were used to confirm a low level of background residue." No quantification of the "low" background is offered. Also, the basalt sample is described as bearing "nearly identical" molecular transfer coefficients (Section V) without the quantified, statistical comparison that should accompany such a statement.



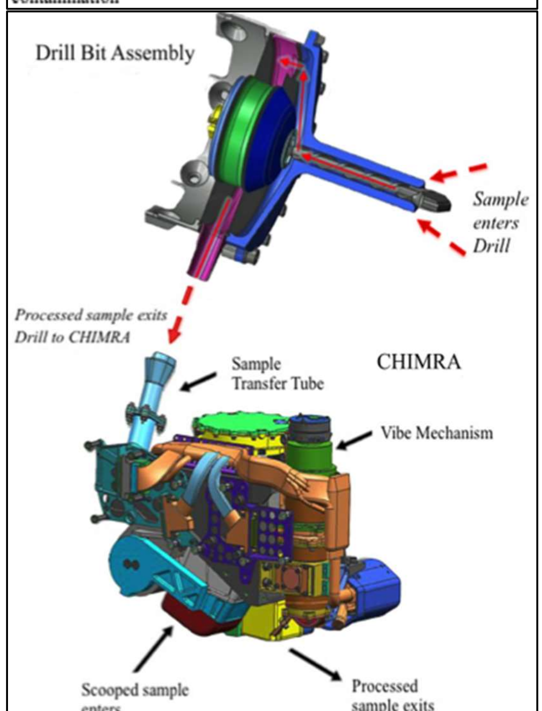


Figure 2: (Top) Sample chamber used in Anderson *et al*, as compared to the complex geometry of the CHIMRA sample handling hardware on MSL (Bottom). Bottom image from Blakkolb *et al* 2014.

d. Geometry-Related Assumptions: One fundamental assumption in DC is uniform distribution of contaminants, as stated in Section III of Anderson *et al* (2012): "Assume that the sample contacting surfaces start out with a uniform contaminant mass per unit area". This is an unrealistic assumption for the complicated geometry of actual sample handling hardware, as contaminants will aggregate at greater concentration in seams, corners, holes, bends, etc. (Figure 2) This assumption is paired with another assumption that the "throw away sample" dilutant will interact uniformly with all surfaces in the sample handling chain. This is probably not a reasonable assumption because sample material will not uniformly interact with seams, corners, holes, bends, etc. The combination of these two assumptions is that contaminants will aggregate to a greater extent in actual sampling hardware than the values presented in Anderson *et al* (2012) suggest.

3) Analytical/On Mars:

a. Implementation: If the sample used to clean the hardware has a greater, or substantially different, carbonaceous content than the actual sample collected, the sample will be contaminated with carbonaceous compounds from the dilutant. This could lead to erroneous science conclusions. Alternatively, if the sample contains a significant fraction of macromolecular carbon then "large" particulates of carbonaceous material may remain in seams, corners, holes, bends, or by static electrical attraction to various surfaces. Anderson *et al* (2012) does not address macromolecular carbon as a contaminant, but this material has been found in martian meteorites (Steele *et al* 2012) and it would constitute the principal form of carbon in meteoritic material delivered to the martian surface. In short, there are significant questions about the relevancy of DC in Mars-relevant conditions that remain unaddressed at present.

This MR finds that DC should not be used for Mars 2020 without first addressing the aforementioned items. The following suggestions for dealing with the problems stated above. First, an independent review of DC could be undertaken, utilizing the range of Tier I compounds, a suitable TOC contaminant suite, and Mars-relevant macromolecular carbon. Standard analytical chemistry practice should be used, to include triplicate measurements, the methods of Ambruster and Pry (2008) or a suitable equivalent, and a thorough statistical treatment of measurement results. Quantitative transfer efficiency values should be calculated for the range of spacecraft materials present in any sample handling system where DC is to be used. DC should be tested in real-world sample handling geometries that include corners, ridges, seams, etc. such that it adequately represents the actual hardware utilized on the mission. Finally, the method should be subjected to a robust peer-reviewed process.

Finding MR6: The "dilution cleaning" method has not been adequately proven for utilization on the Mars 2020 mission. Shortcomings have been identified in terms of peer review, method verification, analytical and testing approach, application to space flight hardware, and performance under martian conditions. The method should be revisited and independently tested using statistically and analytically robust methods, and scrutinized in a rigorous peer review process.

7. Need for Independent Contamination Control Oversight of the Mars 2020 Project

Part 3 of the "Statement of Task" in the OCP charter states that the panel must examine the draft contamination control methods, requirements and verification strategy: "Evaluate draft Mars 2020 mission … draft verification methodologies", and section 3a, "Propose modifications to the draft Mars 2020 requirements and verification methodologies as needed" (OCP Charter document, p.2). The OCP RP states that, "[t]he M2020 contamination control program is expected to be based heavily on heritage MSL practices." (Section 9.5.2.1, p.106). Ergo, examination of the contamination control methods used for MSL is directly applicative to Mars 2020 contamination control.

The MR finds that contamination control for MSL is poorly documented and features errors in execution that would threaten Mars 2020 with mission failure if repeated for that mission. Some outstanding discrepancies are as follows:

1. <u>Significant deviation from panel recommendations (I)</u>: The OCSSG recommended 1 ng/cm^2 of NVR for "Sample handling elements coming in direct contact with samples" (Table 3., OCSSG report, p.15). Instead of complying with this restriction, the OCP PR states, "[t]he Project Team, which included the PI-led SAM instrument Team" made the decision that, "[r]ather than attempt to modify the OCSSG-proposed limits into a set of implementable requirements, the Project proceeded with a waiver against the requirements as-written" (OCP PR p.14). At which point the 1 ng/cm^2 value was no longer an actual requirement is not clear to the OCP panel. The actual value implemented was 100 ng/cm^2, or two orders of magnitude greater contamination than OCSSG recommended [Blakkolb *et al* 2014]. Given the paucity of organic compounds in martian materials as described earlier, a change in contamination control requirements of this magnitude in Mars 2020 would imperil the success of the caching mission. The suggested remedy for this item is to adhere closely to the recommendations of OCP and previous panels, and both adoption of and changes to contamination control requirements should be made in an open forum with direct input from the scientific community.

2. <u>Significant deviation from panel recommendations (II)</u>: The OCSSG and ND-SAG recommended no more than between 10-40 ppb TOC contamination in

samples analyzed by the MSL rover. According to Blakkolb *et al* (2014), the amount of contamination delivered to the first drill-acquired sample was ≤430 ppb, *or more than an order of magnitude greater contamination than the panels recommended.* Blakkolb *et al* (2014) states that this value arose from "a Project decision", indicating that contamination control necessities were disregarded during mission operations. If such a decision is repeated on Mars 2020, the collected sample will be insufficiently clean for inclusion in the cache, and the introduction of such a high level of contamination into the sample handling hardware might imperil the caching mission. The suggested remedy for this item is to include a contamination control official in the operations team with sufficient authority to disallow actions that would imperil the mission.

3. <u>Inadequate contamination control monitoring</u>: Blakkolb *et al* (2014) describes their method of measuring carbonaceous residue from MSL sample handling hardware, which involves a hexane-saturated swab of spacecraft surfaces followed by dichloromethane extraction. The extracted solution was then "evaporated onto KBr" (*ibid*, p.2). The use of hexane as a sampling solvent is problematic in that the solubility of contaminant species is very limited in hexane, making it a poor choice to sample a wide range of environmental contaminants. Sampling the variety of contaminants spelled out in, for example, the Tier 1 list of the OCP, requires solvents capable of dissolving a wide variety of compounds. Hexane is a nonpolar compound that will dissolve and sample only nonpolar or lightly polar contaminants, such as long-chain alkanes, oils, fats, etc. Similarly, hexane rates an eluotropic strength of 0.01 on Snyder's eluotropic series (Snyder 1986), meaning it has negligible ability to extract compounds from ion-exchange resins. It is for this reason that ASTM

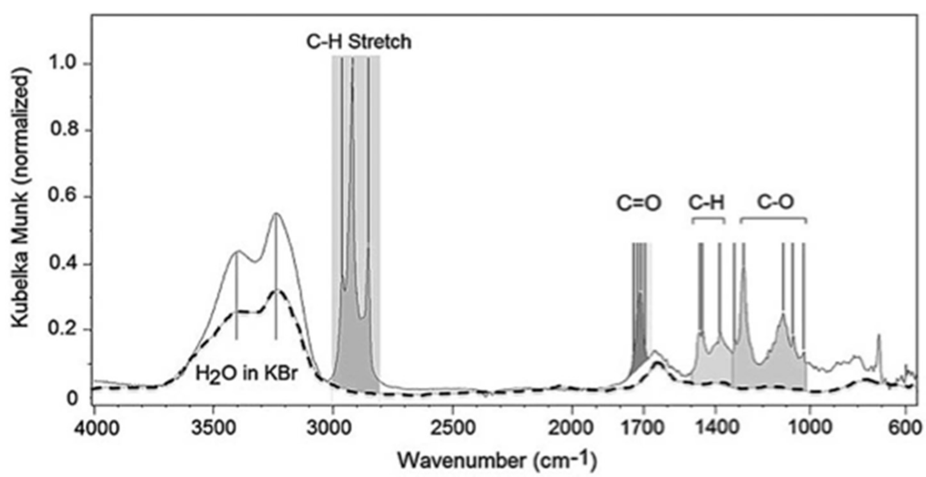


Figure 3: Fig. 3 from Blakkolb *et al* (2014) showing an FT-IR spectrum of contaminants sampled from the MSL sample handling system, collected using hexane-soaked swabs. The spectrum is described as "mainly aliphatic hydrocarbons and esters", consistent with lubricating oils. Notably missing are the variety of polar compounds comprising much of the suite of common environmental contaminants, and which are insoluble in the hexane used for swab sampling.

E1235-12, “Standard Test Method for Gravimetric Determination of Non-Volatile Residue (NVR) in Environmentally Controlled Areas for Spacecraft” prescribes the use of HPLC-grade ethyl acetate or an azeotropic mixture of cyclohexane/ethyl acetate to sample surficial contaminants. It is unclear why this, or similar, standard methods were not adopted for MSL. Results of the hexane-based swabbing indicate that the testing protocol was inadequate. The FT-IR spectrum shown in Blakkolb *et al* (2014) shows “aliphatic hydrocarbons and esters” (*ibid*, p.3), esters comprising many oil-based lubricants such as common cutting fluids. Such compounds are long-chain alkanes with some solubility in hexane. However, missing from the FT-IR spectrum are other common environmental contaminants that can be expected to be present, such as PAHs, common plasticizers to include phthalates, dipicolinic acid, nucleic acids and proteins, amino acids, etc. These compounds are insoluble or poorly soluble in hexane and so were not sampled using the hexane-based sampling method. The MR finds that it is likely that these and other common contaminants were most likely not sampled due to the choice of hexane as a solvent during sampling, are reasonably expected to be present at a concentration on par with that of the “hydrocarbons and esters” noted, and so the Blakkolb *et al* (2014) assessment of contamination concentration in the MSL sample handling system likely underreports the true contaminant population by a significant amount. If this, or similar, errors in contamination control implementation are repeated for the Mars 2020 mission the caching mission will likely be imperiled. The suggested remedy for this item is oversight of the Mars 2020 contamination control process by an agency independent from the spacecraft assembly team.

MSL contamination control was not thorough, effective, or well reported to the degree that will be required for Mars 2020 mission success. The solution to this problem is to implement a standing contamination control review panel that will closely observe and advise all Mars 2020 contamination control procedures, with sufficient authority that their requirements cannot be waived. This panel might remain in effect indefinitely, providing oversight for sample curation of the returned cache.

Finding MR7: The Mars 2020 mission claims considerable heritage from the MSL mission, but MSL contamination control efforts contain errors and implementation discrepancies that would imperil the Mars 2020 caching mission were they repeated. A standing contamination control panel should be formed to provide independent oversight for the Mars 2020 mission.

References

Anderson M., Katz I., Petkov M., Blakkolb B., Mennella J., D'Agostino, S., Crisp J., Evans J., Feldman J., Limonadi D., "In situ cleaning of instruments for the sensitive detection of organics on Mars" *Review of Scientific Instruments* **83** (2012) 105109.

Armbruster D. and Pry T., "Limit of blank, limit of detection and limit of quantification", *Clin. Biochem. Rev.* **29** Suppl. (2008) S50-S52.

Bada, Jeffrey L., Daniel P. Glavin, Gene D. McDonald, and Luann Becker. "A search for endogenous amino acids in Martian meteorite ALH84001." *Science* **279**, no. 5349 (1998): 362-365.

Benner S., Devine K., Matveeva L., Powell D., "The missing organic molecules on Mars", *PNAS* **97**, 6 (2000) 2425-2430.

Blakkolb B., Logan C., Jandura L., Okon A., Anderson M., Katz I., Aveni G., Brown K., Chung S., Ferraro N., Limonadi D., Melko J., Mennella J., Yavrouian A., "Organic cleanliness of the Mars Science Laboratory sample transfer chain", *Review of Scientific Instruments* **85** (2014) 075111.

Biemann, Klaus, John Oro, P. Toulmin, L. E. Orgel, A. O. Nier, D. M. Anderson, P. G. Simmonds et al. "Search for organic and volatile inorganic compounds in two surface samples from the Chryse Planitia region of Mars." *Science* **194**, no. 4260 (1976): 72-76.

Borg, Lars E., Jennifer E. Edmunson, and Yemane Asmerom. "Constraints on the U-Pb isotopic systematics of Mars inferred from a combined U-Pb, Rb-Sr, and Sm-Nd isotopic study of the Martian meteorite Zagami." *Geochimica et cosmochimica acta* **69**, no. 24 (2005): 5819-5830.

Botta O. and Bada J., "Extraterrestrial organic compounds in meteorites", *Surveys in Geophysics* **23** (2002) 411-467.

Boynton, W. V., D. W. Ming, S. P. Kounaves, S. M. M. Young, R. E. Arvidson, M. H. Hecht, J. Hoffman et al. "Evidence for calcium carbonate at the Mars Phoenix landing site." *Science* **325**, no. 5936 (2009) 61-64.

Brown P., Hildebrand A., Zolensky M., Grady M., Clayton R., Mayeda T., Tagliaferri E., Spalding R., MacRae N., Hoffman E., Mittlefehldt D., Wacker J., Bird J., Campbell M., Carpenter R., Gingerich H., Glatiotis M., Greiner E., Mazur M., McCausland P., Plotkin H., Mazur T., "The fall, recovery, orbit and composition of the Tagish Lake meteorite: a new type of carbonaceous chondrite" *Science* **290** (2000) 320-325.

Burnett, D. S., B. L. Barraclough, R. Bennett, M. Neugebauer, L. P. Oldham, C. N. Sasaki, D. Sevilla et al. "The Genesis discovery mission: return of solar matter to

Earth." *Space Science Reviews* **105**, no. 3-4 (2003): 509-534.

Burton, A. S., M. P. Callahan, J. E. Elsila, E. M. Baker, K. E. Smith, D. P. Glavin, and J. P. Dworkin. "Amino Acids from Mars? Clues from the Martian Shergottite Roberts Massif (RBT) 04262." In *Lunar and Planetary Institute Science Conference Abstracts*, vol. **44**, p. 2613. 2013.

Callahan, Michael P., Aaron S. Burton, Jamie E. Elsila, Eleni M. Baker, Karen E. Smith, Daniel P. Glavin, and Jason P. Dworkin. "A search for amino acids and nucleobases in the Martian meteorite Roberts Massif 04262 using liquid chromatography-mass spectrometry." *Meteoritics & Planetary Science* **48**, no. 5 (2013): 786-795

Dreibus, G., F. Wlotzka, W. Huisl, E. Jagoutz, A. Kubny, and B. Spettel. "Chemistry and petrology of the most feldspatic shergottite: Dhofar 378." *Meteoritics and Planetary Science Supplement* **37** (2002): 43.

Glavin, Daniel P., Jeffrey L. Bada, Karen LF Brinton, and Gene D. McDonald. "Amino acids in the Martian meteorite Nakhla." *Proceedings of the National Academy of Sciences* **96**, no. 16 (1999): 8835-8838.

Keiji, Misawa, Yamada Kazuhiro, Nakamura Noboru, Morikawa Noritoshi, Yamashita Katsuyuki, and Wayne R. Premo. "Sm-Nd isotopic systematics of lherzolitic shergottite Yamato-793605." *Antarctic Meteorite Research* **19** (2006): 45-57.

Klein, Harold P., Norman H. Horowitz, Gilbert V. Levin, Vance I. Oyama, Joshua Lederberg, Alexander Rich, Jerry S. Hubbard et al. "The Viking biological investigation: Preliminary results." *Science* **194**, no. 4260 (1976): 99-105.

Kminek, Gerhard, and Jeffrey L. Bada. "The effect of ionizing radiation on the preservation of amino acids on Mars." *Earth and Planetary Science Letters* **245**, no. 1 (2006): 1-5.

Kounaves, S. P., M. H. Hecht, J. Kapit, K. Gospodinova, L. DeFlores, R. C. Quinn, W. V. Boynton et al. "Wet Chemistry experiments on the 2007 Phoenix Mars Scout Lander mission: Data analysis and results." *Journal of Geophysical Research: Planets* (1991–2012) 115, no. E1 (2010).

MacPherson, G., and the Mars Sample Return Science Steering Group II (2005). The first Mars surface-sample return mission: Revised science considerations in light of the 2004 MER results, Unpublished white paper, 68 p, Appendix III of Science Priorities for Mars Sample Return; posted March 2008 by the Mars Exploration Program Analysis Group (MEPAG) at http://mepag.jpl.nasa.gov/reports/ndsag.html

Mahaffy P., Beaty D., Anderson M., Aveni G., Bada J., Clemett S., Des Marais D., Douglas S., Dworkin J., Kern R., Papanastassiou D., Palluconi F., Sinnonds J., Steele A.,

Waite H., Zent A., “Report of the Organic Contamination Science Steering Group”, Unpublished white paper, http://mepag.jpl.nasa.gov/reports/index.html

McDonald, Gene D., and Jeffrey L. Bada. "A search for endogenous amino acids in the Martian meteorite EETA79001." *Geochimica et cosmochimica acta* **59**, no. 6 (1995): 1179-1184.

Ming D., Archer P., Glavin D., Eigenbrode J., Franz H., Sutter B., Brunner A., Stern J., Freissinet C., McAdam A., Mahaffey P., Cabane M., Coll P., Campbell J., Atreya S., Niles P., Bell III J., Bish D., Brinckerhoff W., Buch A., Conrad P., Des Marais D., Ehlmann D., Fairen A., Farley K., Flesch G., Francois P., Gellert R., Grant J., Grotzinger J., Gupta S., Herkenhoff K., Hurowitz J., Leshin L., Lewis K., McLennan S., Miller K., Moersch K., Morris R., Navarro-Gonzalez., Pavlov A., Perrett G., Pradler I., Squyres S., Summons R., Steele A., Stolper E., Sumner D., Szopa C., Teiturier S., trainer M., Treiman A., Vaniman D., Vasavada A., Webster C., Wray J., Yingst R., MSL Science Team, “Volatile and organic compositions of sedimentary rocks in Yellowknife Bay, Gale Crater, Mars”, *Science* **343** (2014) 1245267.

Mustard, J.F., M. Adler, A. Allwood, D.S. Bass, D.W. Beaty, J.F. Bell III, W.B. Brinckerhoff, M. Carr, D.J. Des Marais, B. Drake, K.S. Edgett, J. Eigenbrode, L.T. Elkins-Tanton, J.A. Grant, S. M. Milkovich, D. Ming, C. Moore, S. Murchie, T.C. Onstott, S.W. Ruff, M.A. Sephton, A. Steele, A. Treiman (2013): Report of the Mars 2020 Science Definition Team, 154 pp., posted July, 2013, by the Mars Exploration Program Analysis Group (MEPAG) at http://mepag.jpl.nasa.gov/reports/MEP/Mars_2020_SDT_Report_Final.pdf.

Nakamura, Noboru, Daniel M. Unruh, Mitsunobu Tatsumoto, and Robert Hutchison. "Origin and evolution of the Nakhla meteorite inferred from the Sm-Nd and U-Pb systematics and REE, Ba, Sr, Rb and K abundances." *Geochimica et Cosmochimica Acta* **46**, no. 9 (1982): 1555-1573.

Navarro ‐ González, Rafael, Edgar Vargas, Jose de La Rosa, Alejandro C. Raga, and Christopher P. McKay. "Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on Mars." *Journal of Geophysical Research: Planets* (1991–2012) **115**, no. E12 (2010).

Navarro-González, R., Vargas, E., de La Rosa, J., Raga, A. C., & McKay, C. P. Reanalysis of the Viking results suggests perchlorate and organics at midlatitudes on Mars. *Journal of Geophysical Research: Planets* (2010), 115(E12).

Nyquist, L. E., Y. Ikeda, C-Y. Shih, Y. D. Reese, N. Nakamura, and H. Takeda. "Sm-Nd Age and Nd-and Sr-Isotopic Evidence for the Petrogenesis of Dhofar 378." *30th Symposium on Antarctic Meteorites* (2006).

Nyquist, L. E., D. D. Bogard, C-Y. Shih, J. Park, Y. D. Reese, and A. J. Irving. "Concordant Rb–Sr, Sm–Nd, and Ar–Ar ages for Northwest Africa 1460: A 346Ma old basaltic

shergottite related to "lherzolitic" shergottites." *Geochimica et Cosmochimica Acta* **73**, no. 14 (2009): 4288-4309.

Oro, J., and G. Holzer. "The photolytic degradation and oxidation of organic compounds under simulated martian conditions." *Journal of Molecular Evolution* **14**, no. 1-3 (1979): 153-160.

Pearson V., Sephton M., Franchi I., Gibson J., Gilmour I., "Carbon and nitrogen in carbonaceous chondrites: Elemental abundances and stable isotopic compositions" *Meteoritics and Planetary Science* **41** (2006) 1899-1918.

Pizzarello S., Cronin J., "Non-racemic amino acids in the Murray and Murchison meteorites", *Geochimica et Cosmochimica Acta* **64**, 2 (2000) 329-338.

Pizzarello S., Huang Y., Becker L., Poreda R., Nieman R., Cooper G., Williams M., "The organic content of the Tagish Lake meteorite", *Science* **293** (2001) 2236-2239.

Pizzarello S., Cooper G., Flynn G., "The nature and distribution of the organic material in carbonaceous chondrites and interplanetary dust particles", in Lauretta, Dante S., and Harry Y. McSween, eds. <u>Meteorites and the early solar system II</u>. Vol. 2. University of Arizona Press, 2006.

Rubin, Alan E., Paul H. Warren, James P. Greenwood, Robert S. Verish, Laurie A. Leshin, Richard L. Hervig, Robert N. Clayton, and Toshiko K. Mayeda. "Los Angeles: The most differentiated basaltic martian meteorite." *Geology* **28**, no. 11 (2000): 1011-1014.

Sandford, Scott A., Saša Bajt, Simon J. Clemett, George D. Cody, George Cooper, Bradley T. Degregorio, Vanessa de VERA et al. "Assessment and control of organic and other contaminants associated with the Stardust sample return from comet 81P/Wild 2." *Meteoritics & Planetary Science* **45**, no. 3 (2010): 406-433.

Sephton M., "Organic compounds in carbonaceous meteorites", *Nat. Prod. Rep.* **19** (2002) 292-311.

Snyder L., <u>High-Performance Liquid chromatography</u> (C. Horvàth ed.), Vol. 3, Academic Press, New York (1986).

Steele A., McCubbin F. M., Fries M., Kater L., Boctor N. Z., Fogel M. L., Conrad P. G., Glamoclija M., Spencer M., Morrow A. L., Hammond M. R., Zare R. N., Vicenzi E. P., Siljeström S., Bowden R., Herd C. D. K., Mysen B. O., Shirey S. B., Amundsen H. E. F., Treiman A. H., Bullock E. S. and Jull A. J. T. (2012) A Reduced Organic Carbon Component in Martian Basalts. *Science* **337**, 212–215.

Summons, Roger E., Jan P. Amend, David Bish, Roger Buick, George D. Cody, David J. Des Marais, Gilles Dromart, Jennifer L. Eigenbrode, Andrew H. Knoll, and Dawn Y.

Sumner. "Preservation of Martian organic and environmental records: Final report of the Mars Biosignature Working Group." *Astrobiology* **11**, no. 2 (2011): 157-181.

Appendix A: Discussion of the Nd/AA ratio in martian meteorites.

Neodynium (Nd): The Nd value is from bulk measurements of Nd in Nakhla (Nakamura *et al* 1982), Yamato 793605, (Keiji *et al* 2006), ALH 77005 (Borg *et al* 2001, Keiji *et al* 2006), LEW 88516 (Keiji *et al* 2006), NWA 1950 (Keiji *et al* 2006), Zagami (Borg *et al* 2005), NWA 1460 (0.216 to 11.3 ppm, n=3, Nyquist *et al* 2009), and Dhofar 378 (Dreibus *et al* 2002, Nyquist *et al* 2006). **Whole rock Nd analyses yielded $\mathbf{16\overline{2}0 \pm 11\overline{5}0}$ ppb** (n=18 literature values over eight martian meteorites). Few analyses of martian meteorites have yielded amino acids, but values are reported for EETA79001 (0.4 to 1.0 ppm, n=2, McDonald and Bada 1995; 0.592 ppm, n=1, Glavin *et al* 1998), Nakhla (0.02 to 0.33 ppm, n=2, Glavin *et al* 1999), and ALH84001 (0.074 to 0.1, n=2, Bada *et al* 1998) for **$\mathbf{3\overline{1}0 \pm 3\overline{1}0}$ ppb** (n=7 literature values over three meteorites).

The ratio of Nd/AA averages is 5.2.

Amino acids: Glavin *et al* 1999 states that "The amino acids in Nakhla appear to be derived from terrestrial organic matter that infiltrated the meteorite soon after its fall to Earth, although it is possible that some of the amino acids are endogenous to the meteorite." McDonald and Bada says of the EETA79001 measurement, "**The detected amino acids consist almost exclusively of the L-enantiomers of the amino acids commonly found in proteins, and are thus terrestrial contaminants**." And Bada *et al* 1998 says, "**The amino acids present in this sample of ALH84001 appear to be terrestrial in origin** and similar to those in Allan Hills ice, although the possibility cannot be ruled out that minute amounts of some amino acids such as D-alanine are preserved in the meteorite." Therefore, the true concentration is much less than 310±310 ppb. The RBT 04262 martian meteorite was found to contain a few amino acids of about 90 ppb concentration, but Burton *et al* (2013) finds that "**If these amino acids are extraterrestrial, they could have formed from high-temperature amino acid synthesis either below the Martian surface or during the impact that led to the ejection of the RBT 04262 parent body, or been delivered to the Martian surface from the impactor itself**", and that their composition is consistent with shock-derived synthesis. Callahan *et al* (2013) concurs with this finding. To date, no definitively martian amino acids have been discovered.

Appendix B: Discussion of the Total Carbon/Biosignature-Relevant Carbon Ratio

The 1:1E^6 ratio value comes from the following calculation:

Total redbed carbon: 0.1 to 0.01 wt% total organic carbon (TOC), or 1E^6 to 1E^5 ppb (ng/g); mean value is 5E^5 ppb.

Each "biosignature" species: 1 to 0.1 ppb (ng/g); mean value is 0.5 ppb.

We will express this as a ratio of the mean values for both the upper and lower value:

$\frac{\bar{x}_B}{\bar{x}_{TOC}}$ Where $\bar{x}_B$: The mean amount of biosignature carbon and $\bar{x}_{TOC}$ is the mean TOC value.

$$\frac{5E^5}{0.5} = 1E^6$$

Ergo, for the redbeds example the ratio of each biosignature species to TOC is approximately 1:1E^6.